

PATENT SPECIFICATION

731.116



Date of Application and filing Complete Specification: April 22, 1953.

No. 11114/53.

Application made in Denmark on April 23, 1952.

(Patent of Addition to No. 682,736 dated Oct. 19, 1950).

Complete Specification Published: June 1, 1955.

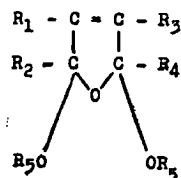
Index at acceptance:—Class 41, B2C.

COMPLETE SPECIFICATION

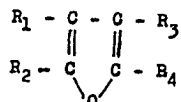
A method for producing 2,5-Dialkoxy-2,5-Dihydrofurans

We, KEMISK VÆRK KØGE A/S, a company organized under the laws of Denmark, of 39, Overgaden neden Vandet, Copenhagen, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Patent No. 682,736 relates to a method for producing 2,5 - dialkoxy - 2,5 - dihydrofurans having the general formula:



where R_1 , R_2 , R_3 , and R_4 are hydrogen, alkyl, aryl, aralkyl, alicyclic or heterocyclic groups, and R_5 is an alkyl group or substituted alkyl group. The said compounds are produced by oxidizing furans having the general formula:



dissolved in a solvent consisting of or containing an alcohol of the general formula R_5OH , where R_5 has the above significance. The characteristic feature of the said method is that the oxidation carried out with an electrolytically produced oxidizing agent, and to this end an electrolyte is used which can be dissolved in the solvent in question and which is preferably a halogen-containing compound which yields free halogen by the electrolysis.

However, it may sometimes be difficult to find a halogen compound which is sufficiently soluble in the solvent in question, and to some

extent this drawback limits the utility of the said method.

It has now been found that a number of different salts are very well suited as electrolytes in the described method, and the modification of said method forming the subject of the present invention is characterized in that the electrolysis is carried out with a nitrate, a thiocyanate, a formate, boron fluoride etherate or a mixture of two or more of these substances or sulphuric acid dissolved in the solvent.

By this extension of the number of suitable electrolytes it will always be possible to find a usable electrolyte or mixture of electrolytes.

The method, which otherwise follows that of the main patent closely, will be illustrated in the following by some examples.

EXAMPLE 1.

5 g. of sodium nitrate are dissolved in 270 ccs. of methanol, and 20 ccs. of furan are added, whereafter the solution is cooled to between -10 and -20° C. and electrolysed at a potential of about 5 volts, 13.4 ampere hours being passed through the solution. On working-up the electrolysate in the manner described in the main patent, the yield is 14.0 g. of 2,5-dimethoxy-2,5-dihydrofuran, boiling at $49-54^\circ$ C. under 10 mm. of mercury.

EXAMPLE 2.

5 g. of sodium formate are dissolved in 255 ccs. of methanol, and 25 ccs. of furan are added whereafter the solution is electrolyzed (consumption of electricity: 7.2 ampere hours) and worked up as described in the main patent. The yield is 3.0 g. of 2,5-dimethoxy-2,5-dihydrofuran, boiling at $52-57^\circ$ C. under 13 mm.

EXAMPLE 3.

5 g. of ammonium thiocyanate are dissolved in 250 ccs. of methanol, and 25 ccs. of furan are added whereafter the mixture is electrolyzed (7.8 ampere hours) and worked up as described in the main patent. The yield is 3.5 g. of 2,5-dimethoxy-2,5-dihydrofuran, boiling at $56-57^\circ$ C. under 18 mm.

[Price 3s. 0d. Price 4s. 6d.]

Price 75p

EXAMPLE 4.

5.0 g. of ammonium nitrate are dissolved in 250 ccs. of methanol, and 20 ccs. of furan are added whereafter the mixture is electrolyzed (12.0 ampere hours) and worked up as described in the main patent. The yield is 8.0 g. of 2,5-dimethoxy-2,5-dihydrofuran, boiling at 48—63° C. under 9 mm.

EXAMPLE 5.

5.0 ccs. of boron trifluoride etherate are dissolved in 260 ccs. of methanol, and 25 ccs. of furan are added whereafter the mixture is electrolyzed (13.7 ampere hours) and worked up as described in the main patent. The yield is 15 g. of 2,5-dimethoxy-2,5-dihydrofuran, boiling at 51—61° C. under 12 mm.

EXAMPLE 6.

1 g. of concentrated sulphuric acid is dissolved in 220 ccs. of methanol and 75 g. of furan, and the mixture is electrolyzed as described in example 1. When 31.6 ampere hours (54 per cent. of the theoretical) have passed the solution, the electrolysis is stopped. The dark brown reaction product is poured into a solution of sodium methoxide (1.30 g. of sodium in 25 ccs. of methanol), and the methanol is distilled off at atmospheric pres-

sure. The residue is distilled in vacuum, and 55 g. of a product are collected which at 16 mm. of mercury distills between 54 and 149° C., some 10—20 g. of a dark residue remaining in the flask. By fractionated distillation at 20 mm. of mercury, 31.7 g. of 2,5-dimethoxy-2,5-dihydrofuran are collected at about 64° C., corresponding to a yield of 41 per cent., calculated on the consumption of electricity.

What we claim is:—

1. In a method for producing 2,5-dialkoxy-2,5-dihydrofurans according to patent No. 682,736 the modification that the electrolysis is carried out with a nitrate, a thiocyanate, a formate, boron fluoride etherate or mixtures of two or more of these substances, or sulphuric acid dissolved in the solvent.

2. A method of producing 2,5-dialkoxy-2,5-dihydrofurans substantially as described in any of the Examples.

3. 2,5-dialkoxy-2,5-dihydrofurans wherever produced by a process as claimed in claim 1 or 2.

For the Applicants,
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52, Chancery Lane, W.C.2.